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# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Procedures and apparatus for Electrodialytic Treatment of Liquids

We, WALLACE TIERNAN INC., a Corporation organized under the laws of the State of Delaware, United States of America, of 25, Main Street, Belleville 9, New Jersey, United

5 States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to procedures and apparatus for effecting changes in concentration of ions in aqueous electrolytic solutions, and in an important specific aspect is particularly directed to procedures and apparatus for demineralizing water for home, industrial or other use.

Water, as obtained from natural sources, often contains substantial concentrations of dissolved salts. Since the presence of these salts is objectionable for many purposes, it is frequently necessary to subject such water to softening or demineralizing treatments prior to use. Familiar examples of such treatments are the softening of hard water to render it suitable for household use, and the demineralizing of water supplies for boilers to prevent accumulation of deposits of salts in the boiler apparatus. In these and other operations it is commonly necessary or at least highly desirable to reduce the ionic content of the water to very low values, for instance to values substantially below 100 parts per million.

Conventional ion-exchange procedures for softening or demineralizing water involve passing the water through one or more beds of solid ion-exchange material, e.g. inorganic ion exchangers such as zeolites, or organic materials such as ion-exchange resins. In these materials, fixed functional groups of one charge type (positive or negative) are neutralized by mobile counter ions, i.e. ions of opposite charge type which are free to move in and out of the material when the material is immersed in the water to be treated. Softening or demineralization of the water proceeds

by exchange of these mobile ions, equivalent for equivalent, for ions contained in the water.

Some ion-exchange water softening treatments merely replace the dissolved salts in the water with other, less objectionable salts, as by exchange of sodium ion for calcium or magnesiuim ion contained in the raw water. However, in many cases reduction of the total dissolved solids content of the water is necessary. Ion-exchange procedures may be employed to accomplish this result as well; but water having an initially very high ionic concentration (e.g. more than 1000 p.p.m. dissolved solids) cannot be economically treated by conventional ion-exchange procedures when a very dilute (e.g. 5 p.p.m.) effluent is required.

A difficulty with all such ion-exchange procedures is that the bed or beds of ion-exchange material become spent or exhausted after a fairly short period of use and must therefore be removed from service and regenerated at frequent intervals. The regeneration of the material, typically involving treatment with chemicals, is inconvenient and relatively expensive. Furthermore, since the water-treating equipment is unavailable for use during the period of regeneration, duplicate or standby equipment must be provided in cases where continuous water-softening treatment is desired.

Desalting of water may also be effected by electrodialysis. A typical simple electrodialysis cell includes three parallel chambers each filled with a flow of water and separated from each other by ion-permeable membranes; the water to be treated is that flowing through the central chamber. Direct electric current, passed through the cell between positive and negative electrodes respectively immersed in the two outer chambers (which thus constitute the anode and cathode chambers of the cell), causes cations in the cell to migrate into the cathode chambers and anions to migrate into the anode chamber thereby deionizing the water in the

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central treating chamber as desired. The membranes may be so-called permselective membranes, selectively permeable to ions of one charge type and relatively impermeable to ions of opposite charge type; i.e. the membrane separating the treating chamber from the cathode chamber may be cation-permselective and that separating the treating chamber from the anode chamber may be anion-permselective. These membranes permit migration of ions from the treating chamber in the directions mentioned above, while at the same time inhibiting counter-migration of anions and cations from the cathode and anode chambers respectively into the treating chamber under the influence of the current.

Such electrodialysis may be practicable for treatment of water having an initially high ionic concentration (i.e. brackish water containing 5,000 p.p.m. to 2,000 p.p.m. total dissolved salts), in cases where the ionic concentration of the effluent treated water, although reduced, is also still relatively high. However, in a cell of the type described the current is conducted through the treating chamber by the water under treatment; and since the conductivity of water decreases with decreasing ionic concentration, the resistance of the cell becomes very high at low values of ionic concentration of the treated water, with the result that uneconomically large values of DC power are needed to accomplish the ionic transport. Hence, use of an electrodialysis cell as described above is not practicable for production of very dilute effluents.

It has been produced for some purposes to provide an electrodialysis cell, with one or more treating chambers each defined on opposite sides by parallel flat membranes of which one is cation-permselective and the other anion-permselective, and with electrodes disposed to provide direct current flow through the cell in a direction transverse to the membranes, wherein the treating chamber or chambers are filled with ion-exchange particles in contact with the membranes. The water under treatment, as before, flows continuously through the treating chamber; but in this cell the ion-exchange particles and the membranes are arranged to provide a continuous, relatively conductive path for current flow and transport of ions through the treating chamber. Since the ion-exchange particles thus serve to reduce the resistance in the treating chamber, water of very low ionic concentration can be treated or produced at reasonably low power input levels.

The desired improvement in cell conductivity in systems of the latter type is dependent, however, on contact between the ion-exchange particles and the membranes. Even small fluid pressure variations on either side of the membranes tend to impair such contact, undesirably increasing the cell resistance and power requirements; therefore the cell

operates effectively only at very small flow rates. Moreover, to attain a high flow rate (as desired for treatment of substantial volumes of water) the chamber-defining membranes should be widely spaced, i.e. the flow rate capacity of the cell varies directly with the spacing between membranes; but the electrical resistance of the described cell is also directly proportional to the distance between membranes, and hence with other factors equal the power requirement for the cell correspondingly varies in direct proportion to the membrane spacing.

Arrangements for changing the ionic concentration of water, such as the ion-exchange and electrodialysis systems described above, may also be used to produce an effluent having an increased concentration of a particular ion or ions, as desired for particular purposes.

The considerations discussed above in connection with use of these systems for demineralizing water are applicable also to the production of such concentrated effluents. When an ion-exchange bed is used to produce a concentrated stream, the product flow must be periodically interrupted for reconversion of the bed to its initial state. Production of a concentrated effluent by electrodialysis is accomplished by transport of ions from a flow of water in a deionizing chamber to a flow in a concentrating chamber, and involves the problems of cell resistance and power requirements referred to above especially when the total ionic concentration of the water in either or both of the latter chambers is low.

An object of the present invention is to provide procedures and apparatus for changing the ionic concentration of aqueous electrolytic solutions, adapted to treat solutions of very low ionic concentration in an advantageously economical and convenient manner and requiring no interruption of treatment for regeneration or like maintenance operations. A further object is to provide such procedures and apparatus for removing ions from water, enabling production of very dilute effluents at high flow rates and with desirably low power requirements, and thereby effecting demineralization of water to such low effluent concentrations more economically than has heretofore been possible. Still another object is to provide effective and economical procedures and apparatus of this type, suitable for such purposes as the softening of water for household use and the demineralization of boiler feed water.

Further objects and advantages of the invention will be apparent from the detailed description hereinbelow set forth, together with the accompanying drawings, wherein:

Fig. 1 is a sectional elevational view of an electrodialysis cell embodying the invention;

Fig. 2 is a view taken along the line 2--2 of Fig. 1;

Fig. 3 is a cross-sectional view of another embodiment of the invention;

Fig. 3a is a cross-sectional view of a further embodiment of the invention;

5 Fig. 4 is a diagrammatic view of a household, water-softening system incorporating a cell of the type shown in Fig. 1; and

10 Fig. 5 is a flow diagram of a system for demineralizing boiler feed water, including cells of the type shown in Fig. 1.

Referring first to Figs. 1 and 2, the apparatus of the invention in the form there shown comprises an axially vertical tubular cell 10 laterally defined by an elongated hollow cylindrical shell 11 (which may be fabricated, for example, of a material such as "Plexiglass," (Registered Trade Mark) i.e. polymethylmethacrylate, or polyvinylchloride) 15 and closed at its upper and lower extremities by end plates 12 and 14. As shown, the ends of the shell are fitted in annular sockets 15, 16 in the latter plates. The cell structure further includes a cylindrical rod 18, also conveniently fabricated of Plexiglass and having a diameter substantially smaller than the internal diameter of the shell 11; this rod extends through the interior of the cell coaxially therewith, the ends of the rod being held in 20 sockets 19, 20 in the end plates. Rubber gaskets 21 and 22 are inserted in the sockets 15 and 19 in the upper end plate 12.

Within the cell is positioned a hollow cylindrical inner electrode 23, closely surrounding and supported by the rod 18 in coaxial relation thereto. A hollow cylindrical outer electrode 24 is similarly secured to and supported by the inner surface of the shell 11, in concentric spaced relation to the inner electrode 23. An axially elongated annular region is thus defined between the inner and outer electrodes in the cell. These two electrodes 23 and 24 may be fabricated of any suitable electrode material, e.g. platinized titanium 40 metal sheet or titanium expanded-metal mesh coated with an equivalent amount of platinum, or any other suitable electrode metals (for instance such as pure titanium or stainless steel) in sheet or expanded-metal mesh form, or graphite. In any event, the anode should be made of material which is not dissolved by the electrochemical reactions that take place when current is passing through the cell, particularly suitable anode materials being platinum, platinized titanium, and graphite. By way of example of the use of graphite, the outer electrode 24 may be a self-supporting hollow graphite cylinder (instead of the structurally supported metal sheet or mesh cylinder 45 shown) or a ring of graphite rods arranged to form in effect a hollow cylinder, it being understood that the terms "hollow electrode" and "hollow cylindrical electrode" as used herein include a hollow electrode comprising 50 such array of rods.

The inner and outer electrodes 23 and 24 are connected to the terminals of a direct current power supply 26. As an illustrative example of cell arrangement having certain advantages for water-demineralizing operation, the inner and outer electrodes are shown as respectively connected to the negative and positive terminals of the power supply so that the inner electrode 23 is the cathode, and the outer electrode 24 is the anode, of the cell; and the further features and structures of the Fig. 1 cell are described below as arranged for demineralizing operation with this cell polarity, i.e. with the inner electrode as cathode.

A pair of cylindrical tubular permselective membranes are positioned in the region between the two electrodes 23, 24, in concentric spaced relation to each other and to the electrodes. The inner one of these membranes, designated 28, is secured at its extremities to the upper and lower end plates of the cell by plastic collars 29 and 30, and is a so-called cation-permselective membrane; i.e. it is fabricated of or incorporates cation-exchange resin and is permeable to cations but substantially impermeable to anions. The outer membrane, designated 32 and similarly secured to the end plates by collars 33 and 34, is an anion-permselective membrane, fabricated of or incorporating anion-exchange resin so as to be selectively permeable to anions. These membranes are hydraulically tight but have high electrical conductivity.

As particularly shown in Fig. 2, the membranes 28 and 32 divide the region between the inner and outer electrodes into three concentric annular chambers each adapted to receive a flow of water. The inner chamber 36, defined between the inner electrode or cathode 23 and the cation-permselective membrane 28, is the catholyte chamber of the cell; the intermediate chamber 37, defined on its inner side by the membrane 28 and on its outer side by the anion-permselective membrane 32, is the deionizing or treating chamber; and the outer chamber 38, defined between the membrane 32 and the outer electrode or anode 24, is the anolyte chamber. Since the membranes 28 and 32 are hydraulically tight, these three chambers are hydraulically isolated from each other; i.e. water cannot flow between the chambers through the membranes.

The deionizing chamber 37 is filled substantially throughout its length with a packed bed 41 of divided solid ion-exchange material, e.g. very preferably adapted to provide both positive and negative mobile ions. By way of example, and as hereinafter further explained, the bed 41 may comprise a mixture of cation-exchange resin particles and anion-exchange resin particles. The bed 41 is in close contact with both membranes 28 and 32, and the individual particles in the bed are in close contact with each other, so that the bed provides a continuous path for flow of electric

current through the chamber 37 between the membranes. Preferably the catholyte chamber 36 is similarly filled with a packed bed 42 of divided solid cation-exchange resin, and 5 the anolyte chamber 38 is also preferably filled with a packed bed 44 of anion-exchange resin particles.

Raw water to be treated is introduced to 10 the upper end of the deionizing chamber 37 through a conduit 46, for downward flow through the chamber 37, and the effluent treated water is discharged from the latter chamber through a second conduit 47. A minor flow of the raw water from the conduit 46 15 is also supplied to the upper end of the anolyte chamber 38, to constitute the anolyte solution therein, through an inlet 49 controlled by a valve 50. In a preferred, but not essential, arrangement, the anolyte solution is withdrawn 20 from the lower end of the chamber 38 and recirculated through a conduit 52 to the upper end of the catholyte chamber 36, and then flows downwardly through the chamber 36 as the catholyte solution, being discharged 25 from the lower end of the catholyte chamber to waste through an outlet 54.

In the operation of the cell for demineralization of water, a continuous downward flow of water is established and maintained in each of 30 these three chambers of the cell, while a continuous flow of direct current is passed through the cell between the outer anode 24 and inner cathode 23. Ions contained in the water to be treated (flowing through the chamber 37) are absorbed into the ion-exchange bed 41 and migrate through the bed under the influence 35 of the current toward the respective electrodes. Thus, cations migrate inwardly toward the cathode 23, and are transported across the cation-permselective membrane 28 into the catholyte chamber 36, while anions migrate outwardly toward the anode 24 and are transported through the anion-permselective membrane 32 into the anolyte chamber 38. In this 40 way ions are removed from the water to be treated, and transported, through the bed 41 and the membranes, out of the chamber 37; hence the water flowing through the chamber 37 is demineralized, and the ionic concentration 45 of the anolyte and catholyte flows in the chambers 36 and 38 is concomitantly increased. Although the current also promotes migration 50 of anions from the catholyte chamber 36 toward the anode, and of cations from the anolyte chamber 38 toward the cathode, the permselective membranes 28 and 32 effectively inhibit such migration of ions from the chambers 36 and 38; consequently, the deionization 55 of water in the chamber 37 is not substantially counteracted by influx of ions from the other two chambers, but can proceed to produce very low effluent concentrations.

At the cathode 23, cations (i.e. including 60 cations transported from the chamber 37) form hydroxides, with liberation of hydrogen gas,

and similarly at the anode 24, anions form acids with liberation of oxygen gas. Thus, for example, if the cell of Figs. 1 and 2 is employed to deionize water containing sodium chlorite, sodium hydroxide and hydrogen form 70 at the cathode, and hydrochloric acid, chlorine, and oxygen form at the anode. The gases liberated at the electrodes are produced in small amounts, and are in the form of minute bubbles which can ordinarily simply be discharged with the waste from the catholyte chamber; hence in cells of moderate size, no special provisions for gas discharge are required, although in very large units a conventional form of separating device (not shown) may be employed to remove the gases 75 from the waste stream and vent them.

In the operation of the cell as described above, after a short initial start-up period an equilibrium state is achieved and is thereafter maintained as long as operating conditions remain constant. Under equilibrium conditions, with a constant cell current, a given influent water flowing continuously through the chamber 37 at a constant rate is reduced 80 in concentration by a constant amount. The extent of reduction in concentration of the water in the chamber 37 is inversely related to the flow rate of the water and directly related to the magnitude of the current through the cell. Thus, if the flow rate is increased while the current is held constant, the amount of reduction in concentration will be lessened; but the reduction in concentration of a particular influent achieved with a given flow rate 85 at a given current level may be attained with a higher flow rate if the current is also sufficiently increased.

The cell of the invention, as operated in the manner described above, provides continuous demineralization of water, e.g. for household, industrial, or other purposes. Since demineralization proceeds by electrodialytic transport of ions from the treating chamber, no interruption of cell operation for regeneration is ever necessary; and the cell can effect larger changes in concentration of the treated stream than is practicable with conventional single pass ion-exchange systems. At the same time, since the ion-exchange bed 41 together with the permselective membranes affords a continuous low-resistance current path across the treating chamber 37, power requirements for the cell are advantageously low even when the concentration of the water under treatment 90 is very small. Thus demineralization of water to very low effluent concentrations (e.g. as low as 5 p.p.m. or lower) can readily and economically be effected by the cell.

The permselective character of the membranes 28 and 32 contributes fundamentally to efficiency and economy of cell operation. It will be appreciated that as demineralization 95 proceeds, anions (such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{OH}^-$ ) existing and formed at the cathode, 100

and cations (such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{H}^+$ ), existing and formed at the anode, will tend to be transported into the treating chamber 37, under the influence of the current flowing across the cell, with undesirable consumption of power; hence the membranes 28 and 32, by inhibiting such ionic transport by virtue of their permselectivity, substantially reduce power losses in the cell.

The concentric cylindrical arrangement of the cell chambers and membranes provides further important advantages especially in enabling economical operation of the cell at high flow rates, as necessary for practical, efficient water treatment for household and industrial purposes. In particular, the cylindrical configuration of the membranes affords markedly superior mechanical stability for the membranes, with the result that the contact between the membranes and the bed 41 required to maintain low cell resistance is not impaired even when the fluid pressure differentials across the membranes are relatively large, as occasioned by high flow rates. Furthermore, although the invention is not limited to this or any other theory, as a consequence of the geometry of the cell the ohmic resistance varies with the logarithm of the ratio of the diameters of the membranes 32 and 28 and consequently this resistance does not increase as rapidly as the radial distance between membranes 28 and 32, with the result that the power required per unit volume of water under treatment, to effect a given concentration change, decreases as the cell dimensions are increased to accommodate larger flow rates.

These and other advantages of the present cell in the foregoing and other embodiments thereof are achieved, as indicated above, by the tubular arrangement of the cell having an outer electrode concentrically surrounding the inner electrode and further having the space between the electrodes divided into a plurality of chambers for receiving aqueous electrolytic solutions by a plurality of tubular permselective membranes disposed in concentric relation to each other and to the electrodes, together with the provision of a bed of ion-exchange material in at least one of the chambers for enhancing electrical conductivity therethrough. The term "tubular membrane" as used herein is to be understood to refer to a membrane in the form of a tube, whether of cylindrical or other configuration, i.e. a membrane which completely laterally surrounds a region internal thereto. Although cylindrical configuration (as shown in Figs. 1 and 2) especially of the two tubular permselective membranes is regarded as unusually advantageous and a special feature of the invention, it is conceived that other cell configurations may be employed and realize a substantial measure of the advantages described especially where the radial distance between the two membranes is substantially uniform around the cell.

It is to be understood also that the electrodes may correspondingly be other than cylindrical in shape and indeed may depart from true cylindrical configuration even when the membranes are themselves cylindrical. Thus, for instance, in the cell of Figs. 1 and 2 the inner electrode 23 could be other than circular (e.g. square) in cross-section, and the outer electrode 24 could similarly be, for example, square or rectangular in cross-section. Also, and as indicated above, either or both these electrodes may comprise several discrete electrode pieces instead of a single continuous electrode body or piece as shown.

Referring now further to the particular embodiment of the invention illustrated in Figs. 1 and 2, it may be explained that the provision of the inner electrode as the cathode, and the outer electrode as the anode, represents an arrangement for minimizing electrode corrosion. This is because the anode is more susceptible to corrosion than the cathode. Since the current density at the outer electrode is lower than at the inner electrode, provision of the anode as the outer electrode reduces anode corrosion.

Another advantage of arranging the cell of Figs. 1 and 2, for demineralizing operation, with the inner electrode as cathode, is that the anion-permselective membrane is then the outermost of the two membranes (as described above) and hence has a larger surface area than the cation-permselective membrane, with the result that the current density on the anion membrane is lower than that on the cation membrane. For optimum efficiency of cell operation, it is in general preferable that the current density on the anion-permselective membrane be as low as possible, i.e. lower than that on the cation membrane, because anion membranes ordinarily have lower exchange capacities than cation membranes and consequently anion membranes have in general higher ohmic resistance than cation membranes (for example, a typical ratio of anion membrane exchange capacity to cation membrane exchange capacity is 2.5:4).

However, it is to be understood that the aforementioned polarity of the Fig. 1 cell may be reversed, so that the outer electrode 24 is the cathode, and in such case, for demineralizing operation, an anion-permselective membrane is used as the inner membrane 28 while a cation-permselective membrane is used as the outer membrane 32. In this event, the outer chamber 38 is the catholyte chamber of the cell and the inner chamber 36 is the anolyte chamber; thus when beds of ion-exchange material are used in these chambers the bed in chamber 38 preferably includes cation-exchange material and that in chamber 36 preferably includes anion-exchange material. Cell operation proceeds as described above except that cations migrate outwardly, and anions migrate inwardly, from the treating chamber

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37. Also, in such case the anolyte effluent (i.e. the solution discharged from inner chamber 36) may be recirculated through the catholyte (outer) chamber 38; this circulation of water  
 5 from the inner to the outer electrode chamber provides a slightly acid condition in the outer compartment which inhibits precipitation of "hard" (e.g. magnesium and calcium) ions therein thus minimizing sludge deposition in  
 10 the outer chamber.

Similarly, the directions of liquid flow through the cell provided by the conduit system shown in Fig. 1 are preferred for optimum cell operation. Thus it is very preferable  
 15 that the flow of water be directed downwardly through the chamber 37, since if the flow were directed upwardly it would tend to back-wash the resin, i.e. to float or suspend the particles,  
 20 which is necessary to provide the desired low-resistance current path through the chamber 37. This is particularly true in cases where a relatively high flow velocity is desired through the treating chamber. In some cases,  
 25 however, it may be desirable to have the flow the other way, i.e. directed upwardly through the chamber 37.

The flow rate through the anolyte and catholyte chambers is ordinarily substantially lower  
 30 than that in the treating chamber 37, e.g. one-tenth that in the latter chamber, being merely sufficient to prevent excessive build-up of ionic concentration in the anolyte and catholyte chambers such as might cause back-diffusion of ions to the treating chamber. Also, especially in the catholyte chamber, excessive concentration of ions (i.e. excessive alkalinity) may result in precipitation of sediment, partially or even completely clogging the bed therein.  
 40 It is further preferred that the flow rate be directed downwardly in these electrode chambers, but this is less important than in the treating chamber because the flow rate in the electrode chambers is, as stated, ordinarily  
 45 low; also, the anolyte and catholyte solutions are relatively highly conductive since they contain substantial concentration of ions, and for that reason the resistance of the anolyte and catholyte chambers would not be unduly increased even if interparticle contact in the beds in those chambers were disturbed by an upward flow of water. Thus upward flow may be provided in the latter chambers if desired.

In addition, it is preferred, as shown, to  
 55 circulate the water from the anolyte chamber through the catholyte chamber. Since acid is produced in the anolyte chamber, this circulation provides the catholyte chamber with a catholyte having an initial pH below 7. The  
 60 low pH of the catholyte liquid thereby provided minimizes scale precipitation, e.g. precipitation of carbonates, sulfates, etc., in the catholyte chamber. However, the cell can also be operated with separate flows through the  
 65 two electrode chambers, i.e. without recircula-

tion of the anolyte effluent through the catholyte chamber.

For control of the pH in the electrode chambers, and specifically to maintain the pH of the influent to the catholyte chamber at a desired value, provision may be made for introducing water to or withdrawing water from the circulating flow of water intermediate the anolyte and catholyte chambers. Thus, for example, in the cell of Figs. 1 and 2 a valved inlet pipe 55a and a corresponding valve outlet pipe 55b may be connected in the conduit 52 between the latter chambers. Raw water may be injected through inlet 55a as a buffer (and/or some of the anolyte effluent solution may be withdrawn through outlet 55b) to hold the pH of the solution entering the catholyte chamber 36 to a desired value. If the polarity of the cell is reversed as described above, corresponding arrangements for injection of buffer water and withdrawal of circulating anolyte effluent may be made in the line through which the electrode solution circulates from the inner to the outer chamber. Such arrangements and procedures for controlling the pH of the catholyte influent may or may not be employed, depending on the desirability and convenience of such control in particular instances.

Since, as stated above, the anolyte and catholyte liquids are themselves relatively conductive, because of their comparatively high ionic concentration, the beds 42 and 44 in these respective chambers may be provided by non-conductive inert materials such as glass beads, although use of ion-exchange materials in these beds is preferred, to enhance conductivity; also, if desired, these beds 42 and 44 may each comprise a mixture of both anion-exchange material and cation-exchange material, although only the cation-exchange material in the catholyte chamber and only the anion-exchange material in the anolyte chamber contribute to enhancement of conductivity. When the beds 42 and 44 are inert, conduction of current through the latter chambers is provided by the anolyte and catholyte liquids, and the beds of inert materials serve merely to equalize the hydrostatic pressure on the membranes. Indeed, in some cases, particularly in cells of short axial length, the beds 42 and 44 may be entirely omitted, the cylindrical configuration of the membranes being sufficient to maintain them in contact with the ion-exchange bed 41 in the treating chamber even when the anolyte and catholyte chambers are filled only with water. When the beds 42 and 44 are inert or are absent, however, the anolyte and catholyte chambers should be relatively narrow, to minimize the length of the current path (and hence the resistance) through these chambers.

To constitute the bed 41 in the treating chamber 37, as well as the beds 42 and 44 in the catholyte and anolyte chambers, it is

- presently preferred to use ion-exchange material in a particle size of about 50 mesh, that is, predominantly of a particle size approximating that selected in a screening separation upon passing through a U.S. standard No. 50 screen, which has roughly 50 openings per linear inch. If the particles are excessively fine, liquid flow through the beds is impeded; on the other hand, if the particles are too coarse, the ionic flow through the beds is undesirably reduced. 5
- The bed 41 in the treating chamber 37 may comprise either anion-exchange or cation-exchange material (e.g. resin) or very preferably both. While a demineralizing cell of the type shown in Figs. 1 and 2 still partakes of the advantages of the invention when the treating chamber bed comprises only a single charge-type ion-exchange material, it is very preferable (for reduction of cell power requirements) that the bed 41 be adapted to provide both positive and negative mobile ions. 10
- As mentioned above, it is also preferred that the beds be composed of ion-exchange resins and in particular that the treating chamber bed 41 comprise anion-exchange resin particles and cation-exchange resin particles. The latter bed is conveniently provided as a physical mixture of the resins; however, it is not necessary that the constituent resins be evenly dispersed throughout the bed, and indeed the anion-exchange and cation-exchange resin particles may even be arranged in separate layers. As an example of the latter arrangement, the bed 41 may be divided into concentric vertical layers of cation-exchange resin and anion-exchange resin, the cation-exchange resin layer being contiguous to the cation-selective membrane 28; the two 15 layers may be separated from each other by a light plastic screen, or a soluble screen which disappears upon operation of the cell, the purpose of the screen being merely to provide discrete layers of the two resins. If the water under treatment in the chamber 37 should channel in the layers, the cations in the water in the anion-exchange layer and the anions in the water in the cation-exchange layer will nevertheless migrate through the 20 solution; this may to some extent raise the resistance of the cell and increase power requirements, but the power requirement of the present cell is so low that such increase would not detract significantly from economical 25 operation.
- The cation-exchange resin particles and anion-exchange resin particles in the bed 41 (whether provided in mixture, or arranged in layers) may be present in substantially equal proportions by volume, or in other relative proportions, depending in particular on the 30 ionic content of the raw water to be treated and the desired pH of the effluent treated water. While the pH of the treated effluent varies 35 depending on operating conditions with a bed
- of any given composition, it is found that the ratio of anion-exchange resin to cation-exchange resin present in the treating chamber bed is among the factors determining such effluent pH. Thus, for example, in the deionization of water containing sodium sulfate, provision of a treating chamber bed comprising cation-exchange resin and anion-exchange resin in substantially equal parts by volume tends to reduce the pH of the treated water and hence to result in an acid effluent which is undesirable for many purposes. On the other hand, use in the treating chamber of a bed containing 30% cation-exchange resin and 70% anion-exchange resin (by volume) tends to increase the pH of sodium sulfate-containing water during demineralization, at least when the effluent concentration is low. 40
- In general, it is preferred for usual water purification to provide the anion-exchange and cation-exchange resins in the bed 41 in such relative proportions so as to produce a neutral effluent. The optimum proportion of resins for this purpose is dependent on the ionic content of the water to be treated as well as on other factors, e.g., the nature of the membranes used, and conditions of operation; in some cases, as in the demineralization of water containing carbonate or bicarbonate ions, it may be necessary to employ more cation-exchange resin than anion-exchange resin in the bed 41 to achieve a neutral effluent. For treatment of water of any given ionic content, such optimum proportions can readily be determined by simple tests using ion-exchange beds having cation and anion-exchange resins in various ratios. 45
- Any suitable ion-exchange resins may be used in the mixed bed 41 (as well as in the catholyte and anolyte beds 42 and 44). It is particularly preferred to employ synthetic ion-exchange resins; and of these, strong acid cation-exchange resins and strong base anion-exchange resins are preferred, as it is desirable to use highly ionized resins, and the stronger the acid or base, the more highly ionized is the resin. Resins particularly suitable for the bed 41 are sulfonic-acid type cation-exchange resins and quaternary-ammonium type anion-exchange resins. By way of specific example, the bed 41 may consist of a mixture of Ionac C-240 cation nuclear sulfonic strong acid resin and Ionac A-540 anion quaternary-ammonium strong base resin, both these resins being commercially available from Ionac Chemical Company. 50
- Examples of other cation-exchange resins suitable for use in the cell of Figs. 1-2 include phenolic resins containing methylene sulfonic strong acid groups such as the resins C-3 and C-10 manufactured by Chemical Process Company and "Zeo-Karb" (Registered Mark) manufactured by the Permutit Company; polystyrene resins containing nuclear sulfonic strong acid groups such as resins C-20, 55

- C—20X10, C—20X12 and C—25 manufactured by Chemical Process Company, resins 50, 50—X10 and 50—X12 manufactured by Dow Chemical Company, resin C—240 manufactured by Ionac Chemical Company and resins IR—120, IR—122 and IR—124 manufactured by Rohm and Haas Company; acrylic resins containing carboxylic groups, e.g. "Amberlite" (Registered Trade Mark) IRC—50 manufactured by Rohm & Haas Company and "Zeo-Karb" 226 manufactured by Permutit Company; and resins containing phosphorous acid, phosphonic acid and phosphoric acid groups such as resins ES—62, ES—63 and ES—65 manufactured by Chemical Process Company. Examples of other suitable anion-exchange resins include styrene resins containing quaternary-ammonium strong base groups, e.g. "Amberlite" IRA—400, IRA—401 and IRA—410 manufactured by Rohm & Haas Company, "Dowex 1 (Nalcite" (Registered Trade Mark) SBR) and "Dowex 2 (Nalcite" SAR) manufactured by Dow Chemical Company, "Duolite" Registered Trade Mark A—101 and A—102 manufactured by Chemical Process Company, and "Permutit" (Registered Trade Mark) S—1, S—2 and FF resins manufactured by Permutit Company; styrene resins containing weak base groups, e.g. "Amberlite" IR—45 manufactured by Rohm & Haas Company and Dowex 3 manufactured by Dow Chemical Company; phenolic resins containing weak base groups (secondary and tertiary amine) e.g. "Amberlite" IR—4B manufactured by Rohm & Haas Company, and "Duolite" A—114, "Duolite" A—4 and "Duolite" A—7 resins manufactured by Chemical Process Company. The numerical type designations of resins mentioned above are as understood from information heretofore available in the industry.
- While cation-exchange resins and anion-exchange resins, as exemplified by the materials mentioned above, are presently preferred for the beds of the present cell, other ion-exchange materials may also be employed; for example, sulfonated coal, or inorganic cation-exchange materials such as zeolites may be used to provide the cation-exchange constituents of the beds. Also, the bed 41 in the chamber 37 may be constituted of a material providing both positive and negative mobile ions, such as a bipolar resin. A bipolar resin is a resin having both cation and anion-exchange groups; these groups can be trapped one inside another (providing a so-called "ion-exchange alloy") by polymerizing a cation exchanger inside an anion-exchange resin, or they can be chemically bonded to the same polymeric structure. One example of a bipolar resin suitable for use in the bed 41 is the resin designated AG 11A8, manufactured by Bio-RAD Laboratories, which is understood to be prepared by polymerizing an acrylic acid (cation exchanger) inside the "Dowex" 1 (Dow Chemical Company) anion-exchange resin, to provide both cation and anion-exchange sites so that the resin will absorb both anions and cations from solutions with which it comes in contact.
- The permselective membranes 28 and 32 may be any suitable cation-permselective and anion-permselective membranes, respectively; thus they may be either heterogeneous membranes, wherein an ion-exchange resin is dispersed into a matrix (usually a film-forming type of plastic, parchment paper, or fabrics impregnated with mixtures of resin and polymers), or homogeneous membranes, which are obtained ordinarily either by chemical reactions between the active groups and the polymeric matrix, or by dissolving the active ion-exchange materials and the polymeric matrix in a common solvent (interpolymer technique).
- Particular examples of membranes suitable for use as the membranes 28 and 32 in the cell of Figs. 1—2 are the Ionac MC—3142 cation-permeable membrane and the Ionac MA—3148 anion-permeable membrane both commercially available from Ionac Chemical Company. These are heterogeneous membranes, which are understood to be prepared by suspending particles of ion-exchange resins in a solution of a polymer dissolved in a solvent and impregnating this suspension onto a fabric matrix; both membranes are understood to have the following approximate composition:

	Weight %
Ion-exchange resin	30.0
Binder matrix	30.0
(polymethyl-methacrylate)	
Fabric ("Dacron") (Registered Trade Mark)	40.0

- 100 Transport numbers for these membranes have been determined as 0.938 for the MC—3142 and 0.888 for the MA—3148. Other properties

given for these membranes by the manufacturer are as follows:

## MC-3142 MA-3148

Area resistance (ohms-cm <sup>2</sup> )		
in 0.1N NaCl	15	56
in 1.0N NaCl	11	22
Thickness (mils)	6	7
Burst strength (psi)	190	190
Water permeability (ml/hr/ft <sup>2</sup> at 10 psi)	2.4	0
Capacity (milliequivalent/cm <sup>2</sup> )	0.021	0.012
Stability		
Dimensional	Good	Good
Acid	Good	Good
Alkali	Poor	Poor
Drying-Rewetting	Good	Good
Salt	Good	Good
Oxidizing Agents	Good	Good

- Other examples of heterogeneous membranes suitable for use in the present cell include "Permaplex" (Registered Trade Mark) C-20 and "Permaplex" A-20 manufactured by Permutit Company, which are understood to be prepared by the incorporation of sulfonic acid cation-exchange resins or quaternary-ammonium anion-exchange resins into a polymer, e.g. polyethylene, polyvinyl chloride, rubber or other polymers or elastomers; Ionac XLMC-3235 and XLMA-3236 membranes manufactured by Ionac Chemical Company, which are understood to be fabric-supported membranes in which polypropylene is the supporting fabric; the CM-10 and AM-10 fabric supported membranes manufactured by Asahi Glass Company, Yokohoma, Japan; the C-15 and A-15 membranes manufactured by Permutit Company, which are understood to be fabricated by treating a heavy paper with a mixture of phenol, phenolsulfonic acid and formaldehyde followed by condensation reaction (to produce the cation membrane, guanidine being used as the active material to produce the anion-permeable membrane); and the TCX-1, TCX-2, TCX-3 and TCX-4 fabric-supported membranes manufactured by Toyo Soda Manufacturing Company, Tokyo, Japan.
- Examples of homogeneous membranes suitable for use in the cell of Figs. 1-2 include membranes C and A manufactured by Asahi Chemical Industries, Tokyo, Japan; Nalfilm 1, Nalfilm 2, Nalfilm 3, and Nalfilm 4 manufactured by the Nalco Chemical Company; membranes C-60 and A-60 manufactured by CTI-TNO, of the Hague, Netherlands, which are understood to be prepared by swelling a polyethylene sheet in a mixture of styrene and divinyl benzene, carrying out the polymerization at an elevated temperature followed by sulfonation or amination to produce the desired (cation-permeable or anion-permeable) membranes; C-103-C, A-104-B, C-312, C-110-C and A-110 manufactured by American Machine and Foundry Company; membranes C and A produced by Imperial Chemical Industries of London; and membranes CR-61A and AR-11A manufactured by Ionics Incorporated of Cambridge, Massachusetts, which are understood to be fabricated by copolymerization technique wherein styrene and divinyl benzene are copolymerized in the presence of toluene, the copolymerization being carried out in the presence of a fabric or later cast upon the fabric and the usual chemical procedures being employed to introduce fixed ionic groups.
- Although the cell of Figs. 1-2 has been specifically described above as arranged and operated for demineralization of water, it is to be understood that in a broad sense the procedures and apparatus of the present invention have general application in effecting

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transfer of ions to or from aqueous electrolytic solutions (including water of high purity), and in all such cases have special advantages from the standpoint of economy, particularly 5 in affording effective ion transfer with low power requirements where one or more of the streams passing through the cell are highly dilute.

Thus for example, a cell having the structure shown in Figs. 1-2 may be arranged, in accordance with the invention, to produce a concentrated effluent from the treating chamber 37, i.e. for use in cases where it is desired to concentrate one or more ions in an 10 aqueous electrolytic solution. In this instance, utilizing a cation-permselective inner membrane 28 and an anion-permselective outer membrane 32, the inner electrode 23 is connected as the anode of the cell and the outer electrode 24 is connected as the cathode. The aqueous electrolytic solution or solutions (not necessarily the same as the solution in the 15 treating chamber 37) which serve as the source of ions flow through the inner and outer cell chambers 36 and 38, while the stream in which the ions are to be concentrated flows through the treating chamber 37. Under the influence of the current, cations migrate from the inner electrode chamber 36 through the 20 cation-permselective membrane 28 to the treating chamber while anions migrate from the outer electrode chamber 38 to the treating chamber through the anion-permselective membrane 32; at the same time, the permselectivity of the membranes inhibits migration of ions out of the treating chamber. In 25 this manner, the ions are concentrated in the treating chamber stream to produce the desired concentrated effluent.

Further, in accordance with the invention, in the concentrating cell just described one or more of the cell chambers is substantially filled with a packed bed of ion-exchange material, to enhance the conductivity through such 30 chamber or chambers. By way of specific example, to enable one or both of the ion-source solutions flowing through the inner and outer chambers 36 and 38 to be diluted to very low concentration levels during passage 35 through the cell, yet with low cell power requirements, beds of ion-exchange material (i.e. corresponding to the beds indicated at 40 42 and 44) are provided in one or both of these chambers. The charge type or types of ion-exchange material employed in these beds are preferably selected to effect the desired 45 ionic transport through the respective chambers; e.g. the bed 42 in chamber 36 may comprise cation-exchange resin or a mixture of cation and anion-exchange resins, while the bed 44 in chamber 38 may comprise anion-exchange resin, or again, a mixture of the two types. A bed of ion-exchange material 50 (or of inert particles, to equalize hydrostatic pressure on the membranes) may also, if de-

sired, be provided in the treating chamber 37.

In the concentrating cell it is advantageous, for current efficiency, that the inner electrode be the anode, because in such cases the anion membrane is the outer membrane and hence has a larger area (with correspondingly lower current density) than the cation membrane. However, the concentrating cell may also be arranged to operate with the outer electrode as anode; in this event, for concentrating operation a cation-permselective membrane is used as the outer membrane 32 and an anion-permselective membrane is used as the inner membrane 28.

Referring now to Fig. 3, there is shown in horizontal cross-section another embodiment of the invention. The cell of Fig. 3 is generally similar in construction to that shown in Figs. 1-2, and thus includes an axially vertical shell 11 within which inner and outer cylindrical electrodes 23, 24 are disposed in concentric spaced relation and respectively supported by a central rod 18 and by the shell. This cell, however, further includes a plurality of tubular, e.g. cylindrical cation-permselective membranes and a plurality of tubular, e.g. cylindrical, anion-permselective membranes, disposed in the annular region intermediate the inner and outer electrodes, in concentric spaced relation to each other and to the electrodes. In this array of membranes, the cation-permselective membranes alternate with the anion-permselective membranes so that adjacent membranes are respectively selectively permeable to ions of opposite charge types; specifically, the inner electrode 23 is surrounded by a cation-permselective membrane 56, which is successively followed by an anion-permselective membrane 57, cation-permselective membrane 58, anion-permselective membrane 59 and cation-permselective membrane 60.

These membranes 56-60 divide the annular region between the electrodes into six concentric annular chambers for receiving water. The innermost chamber, designated 62, is the catholyte chamber of the cell, and the outermost chamber, designated 63, is the anolyte chamber, the inner and outer electrodes of the cell being connected to a suitable DC power supply (not shown) so that the inner electrode constitutes the cathode of the cell. The four chambers intermediate the inner and outer chambers are each bounded on one side by a cation-permselective membrane and on the other by an anion-permselective membrane.

Proceeding radially outward from the catholyte chamber 62, the intermediate chambers of the cell comprise a first deionizing chamber 64, bounded on its inner side by the cation membrane 56 and on its outer side by the anion membrane 57; a first concentrating chamber 65, bounded on its inner side by the membrane 57 and on its outer side by the cation membrane 58; a second deionizing

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- chamber 66, bounded on its inner side by the membrane 58 and on its outer side by the anion membrane 59; and a second concentrating chamber 67, bounded on its inner side by the membrane 59 and on its outer side by the cation membrane 60. Thus, in short, there are two deionizing chambers 64 and 66, each bounded on its inner side by a cation membrane, and separated from each other by the concentrating chamber 65; and there are two concentrating chambers 65 and 67, each bounded on its inner side by an anion membrane, and separated from each other by the deionizing chamber 66.
- Each of the deionizing chambers 64 and 66 is substantially filled with a packed bed of divided solid ion-exchange material very preferably adapted to provide both positive and negative mobile ions, and conveniently comprising a mixture of cation-exchange resin particles and anion-exchange resin particles; i.e. these beds, respectively designated 70 and 71, may be of the same composition as the bed 41 of the demineralizing cell of Fig. 1, and the considerations relating to bed composition discussed above for the latter bed are equally applicable to these beds. The beds 70 and 71, like the bed 41 in Fig. 1, are contiguous to the chamber-defining membranes and serve to reduce the resistance in the deionizing chambers by providing a path for current flow and ionic transport.
- The concentrating chambers 65 and 67 are also preferably filled with packed beds 72, 73 of divided solid material, to equalize the hydrostatic pressure in these chambers with that in the deionizing chambers. Although the beds 72, 73 may be composed of ion-exchange material, e.g. a mixture of cation and anion-exchange resins similar to that in the beds 70 and 71, to enhance conductivity in the concentrating chambers, the ionic concentrations of the solutions in the latter chambers (as hereinafter more fully explained) are ordinarily of such magnitude that the solutions themselves have relatively high conductivity; hence the beds 72, 73 in the concentrating chambers may be composed of inert material such as glass beads. As in the case of the cell of Figs. 1-2, the catholyte and anolyte chambers 62 and 63 are preferably filled with packed beds 74, 75 of divided solid cation and anion-exchange resins, respectively, although again the beds 74, 75 may be composed of inert material such as glass beads or may in some cases be omitted entirely.
- In the operation of the cell of Fig. 3, continuous flows of water are passed (very preferably in a downward direction) through the six chambers of the cell, while direct current is continuously passed through the cell. This current promotes migration of cations inwardly toward the cathode, and of anions outwardly toward the anode, in each of the cell chambers. In the first deionizing chamber 64,
- cations from the water flowing therethrough are transported through the cation-permselective membrane 56 into the catholyte chamber 62, while anions are transported through the anion-permselective membrane 57 into the first concentrating chamber 65. Similarly cations migrate from the second deionizing chamber 66 through the cation-permselective membrane 58 into the chamber 65, and anions migrate from the chamber 66 through the anion-permselective membrane 59 into the second concentrating chamber 67. Cations migrate into the chamber 67 from the anolyte chamber 63 through the cation-permselective membrane 60.
- Migration of cations and anions from the concentrating chambers 65 and 67 in this cell is substantially prevented, because, as stated, the current promotes inward migration of cations and outward migration of anions; and the inner wall of each of the concentrating chambers is an anion-permselective membrane, substantially impermeable to cations, while the outer wall of each of these chambers is a cation-permselective membrane, substantially impermeable to anions. Consequently, the water passing through the deionizing chambers 64 and 66 in demineralized or reduced in ionic concentration, in the same manner as the water passing through the treating chamber 41 of the cell of Figs. 1-2 and at the same time the water flowing through the concentrating chambers 65 and 67 increases in ionic concentration.
- The cell of Fig. 3 may be employed to effect either demineralization or concentration of water, i.e. either the effluent from the deionizing chambers 64 and 66, or that from the concentrating chambers 65 and 67, or both effluents, may constitute the desired product. In either event, the deionized effluent and the concentrated effluent are discharged separately from the cell. The anolyte and catholyte streams are preferably discharged from the lower end of the cell, mixed together, and then recirculated through the anolyte and catholyte chambers.
- As will be appreciated, the cell of Fig. 3 operates in a manner similar to that of Figs. 1-2 and affords like advantages. By way of further illustration of the operation of the cell of Fig. 3, for deionization of water, flows of raw water may be introduced to the upper ends of the several chambers of the cell for downward flow therethrough; the effluents from the two deionizing chambers are discharged together as the desired demineralized product. In such operation the two deionizing chambers operate in parallel, treating separate flows of the raw water. Alternatively, the deionizing chambers may be operated in series, with raw water supplied to only one of the deionizing chambers and the effluent of that chamber then circulated through the other; in this arrangement, approximately half of the

- desired reduction in concentration may be accomplished in the first deionizing chamber and half in the second, and the effluent of the latter is the product demineralized water.
- 5 Similarly, the concentrating chambers may be operated either in parallel or in series for production of a concentrated product water. Furthermore, such parallel or series arrangement could be operated with either downward and/or upward flows, in the deionizing chambers, concentrating chambers, and electrode chambers.
- 10 It will be understood that the cell of Fig. 3 is exemplary of multi-chamber cells constructed in accordance with the present invention; cells having a larger number of treating chambers may be provided by including additional membranes between the inner and outer electrodes.
- 15 20 Still another cell arrangement in accordance with the invention is shown in cross-sectional view in Fig. 3a. The cell of Fig. 3a again includes an inner electrode 23 shown as supported on rod 18 and outer electrode 24 concentrically surrounding the inner electrode in spaced relation thereto and shown as supported by shell 11. In this embodiment, however, the region between the electrodes is divided into two concentric annular treating chambers 76, 77 (each adapted to receive a flow of aqueous electrolytic solution) by a single tubular cylindrical permselective membrane 78 disposed intermediate the inner and outer electrodes in concentric spaced relation to the electrodes. The membrane 78 may be either anion-permselective or cation-permselective depending on the manner in which the cell is to operate, as hereinafter further explained.
- 25 30 35 The cell of Fig. 3a may be used in a variety of operations to transfer some particular ion from a solution flowing through one of the chambers 76, 77 to a solution flowing through the other chamber. Examples of such operations are the recovery of sulfuric acid from a spent pickling bath and the recovery of chromium from a spent plating bath. As a specific instance of the first mentioned operation, the electrodes of the Fig. 3a cell are connected to a suitable direct current supply so that the inner electrode is the anode, the membrane 78 being an anion-permselective membrane. A stream of spent pickling bath containing iron sulfate ( $\text{FeSO}_4$ ) is advanced through the outer chamber 77,
- 40 45 50 55 60 while the aqueous stream in which the sulfuric acid is to be collected passes through the inner chamber 76. Under the influence of the current, anions ( $\text{SO}_4^{2-}$ ) migrate from the outer chamber to the inner chamber, and thus sulfuric acid collects in the inner-chamber stream as desired.
- The outer chamber 77, for such operation, is substantially filled with a packed bed 79a of divided solid ion-exchange material, e.g.
- 65 ion-exchange resin, very preferably including

at least anion-exchange material (or material providing negative mobile ions). This bed provides enhanced conductivity in the chamber 77 enabling very extensive depletion of ions in the chamber 77, i.e. permitting the pickling bath concentration to be reduced to a very low level, with advantageously low cell power requirements. The cylindrical configuration of the membrane 78 provides mechanical stability resulting in maintained bed-membrane contact even at high flow rates, and thus the membrane configuration together with the provision of the bed affords advantageously efficient and economical cell operation. A further bed 79b, either of ion-exchange resin or of inert material (to equalize hydrostatic pressure on the membrane) may if desired be provided in the inner chamber 76, substantially filling the latter chamber.

It will be appreciated that in the cell of Fig. 3a the polarity may be reversed (so that the outer chamber is the anode) and for recovery of cations in the concentrating stream the membrane 78 may be a cation-permselective membrane; the inner or outer chamber may be used as the diluting chamber, depending on cell polarity and the polarity of the ion to be transferred, but in either event at least the diluting chamber is filled with a packed bed of ion-exchange material, as described above.

As a particular example of use of the present invention, there is shown in Fig. 4 a household water supply demineralizing unit incorporating a cell 10 of the type shown in Figs. 1-2. In this system, raw hard water is introduced through a conduit 80 to a sand and gravel filter 82. The filtered water is then advanced through conduit 46 to the treating chamber 37 of the cell 10, a minor flow of the filtered water also being supplied to the anolyte chamber 38 from the conduit 46 through inlet 49. The cell 10, powered from the rectifier 26, demineralizes the water in the manner described above in connection with Figs. 1-2. The treated water is delivered from the chamber 37 through conduit 47 to a storage tank 83; the anolyte flow is recirculated to the catholyte chamber 36 through conduit 52 and this flow is discharged to waste from the latter chamber through conduit 54. When the water in the tank 83 reaches a predetermined upper level therein, high level control 85 associated with the latter tank actuates a high level switch 86 to shut off a valve 87 in the raw water inlet conduit 80 and also to shut off the electrical power supply to the rectifier 26, so as to halt operation of the system until the level in the tank 83 is reduced by withdrawal of water for use.

From the tank 83, a service pump 88 takes suction through a conduit 89 to deliver water from the tank 83 through a further conduit 90 to a pressure tank 92. The water flows through the tank 92 in such manner that when the

pressure in tank 92 falls below a predetermined level, a pressure switch 94 starts the pump 88, to deliver water to the pressure tank until the pressure builds up again to a predetermined value in tank 92. The pressure switch 94 then shuts off the pump 88. Treated water is delivered from the pressure tank to service through conduit 95.

Although for simplicity of illustration a single cell 10 is shown in the system of Fig. 4, a plurality of such cells may be employed and connected to treat incoming raw water either in series or in parallel; i.e. the raw water flow may be divided among several cells or passed successively from one cell to another. The number of cells to be used in a particular system is dependent on the capacity of the individual cells and the desired total capacity of the system.

Fig. 5 illustrates diagrammatically another system employing the cell of the present invention, arranged as a continuous demineralization unit for use in the treatment of boiler feed water, i.e. to provide a demineralized water supply for a boiler. In this system, raw water to be treated is supplied to a conventional degasifier 98 for removal of dissolved carbon dioxide; a stream of air is blown into the lower portion of the degasifier and a gaseous mixture of carbon dioxide and air is vented at the top of the degasifier. Approximately 95% by weight of the dissolved carbon dioxide is removed from the water in this manner. The water is then chlorinated to destroy organic matter, and the chlorinated water is advanced to a coagulator 100, where it is coagulated chemically with lime and alum; this operation partially softens the water, reducing total hardness by approximately 60%.

The coagulated and partially softened water passes to a clear well 102 from which transfer pumps 104 take suction, advancing the water to and through sand and gravel filters 106. The filtered water from the filters 106 is then introduced to a plurality of the cells 10 of the present invention, where it is demineralized in the manner above described in connection with Figs. 1-2. These cells 10 may be connected in parallel, as shown, the stream of water being divided between them, or may alternatively be connected in series, the stream being passed successively through the several cells. It will be appreciated that in the system of Fig. 5 the degasifier 98, coagulator 100, clear well 102, transfer pumps 104 and sand

and gravel filters 106 represent a conventional arrangement for pretreating boiler feed water before demineralization, and the cells 10 replace the array of ion-exchange units conventionally employed to effect such demineralization.

By way of further illustration of the invention, there are set forth below specific examples of operation of a cell constructed as shown in Figs. 1-2, for demineralization of water containing dissolved sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). In this cell, the inner and outer electrodes were platinated titanium tubes each 12 inches long, the cathode being 1 inch in diameter and the anode being  $2\frac{1}{2}$  inches in diameter. The cation-permeable membrane was formed of Ionac MC-3142 cation membrane, and was  $1\frac{1}{2}$  inches in diameter and 12 inches long; the anion permeable membrane was formed of Ionac MA-3148 anion membrane, and was 2 inches in diameter and 12 inches long. The mixed bed in the treating chamber was provided by a mixture of Ionac C-240 cation nuclear sulfonic strong acid resin and Ionac A-540 anion quaternary ammonium strong base resin; the catholyte bed consisted of Rohm & Haas IR-200 cation-exchange resin and the anolyte bed consisted of Rohm & Haas IRA-400 anion-exchange resin.

#### EXAMPLE I.

Using in the treating chamber a mixed bed consisting of anion-exchange resin and cation-exchange resin in equal parts of volume, a series of demineralization runs were performed in the above-described cell under various conditions. In each case the influent water to the treating chamber contained 500 p.p.m. dissolved  $\text{Na}_2\text{SO}_4$ . For each run, the current density at the cathode was set and maintained at a constant predetermined value and the water to be demineralized was passed continuous flow through the treating chamber, the flow rate being adjusted until the concentration of the effluent became constant at a predetermined value. The flow rate providing such constant effluent concentration was the equilibrium flow rate. Data obtained in each run, including cathode current density, total current through the cell, equilibrium flow rate, and voltage across the cell, and calculated values of power consumed (in kilowatt hours per thousand gallons of water treated), coulomb efficiency, and apparent effluent concentration, are set forth in Table 1:

TABLE 1

Run	I	II	III	IV	V	VI
Current Density at Cathode (amp./ft <sup>2</sup> )	5	10	15	20	30	40
Current (amps)	1.3	2.62	3.9	5.25	7.85	10.4
Flow Rate (gallons per hr.)	1.1	1.38	2.08	2.36	3.45	4.97
Voltage (V.)	14	18	23	24	28	30
Power Consumed (KWH/1000 G.)	16.5	34.2	43.6	53.4	63.7	62.8
Coulomb Efficiency (%)	67	44	37	32	31	33.6
Apparent Effluent Concentration (p.p.m.) (within error of $\pm 1/2$ p.p.m.)	5	5	1	5	5	5

For purposes of comparison, a run was performed, under conditions similar to run I above, in a conventional filter-press type of electrodialyzer; power consumption in the latter electrodialyzer was found to be about 110 KWH/1000 G. and the coulomb efficiency was approximately 21%. In a further comparison run, water containing 500 p.p.m dissolved Na<sub>2</sub>SO<sub>4</sub> was deionized in a convention-

al electrodialysis unit to an effluent concentration of 5 p.p.m., with a cathode current density of 10 amps./ft<sup>2</sup> as in run II above. The conventional unit has a total membrane area of 4 square feet whereas the abovedescribed cell of the present invention had a total membrane area of 0.92 square feet. Results in the conventional unit are compared with run II above in Table 2:

TABLE 2

	Conventional Unit	Run II
Voltage (v.)	210	18
Current (amp.)	3.4	2.62
Power (W.)	714	47.2
Flow Rate (GPH)	4.7	1.38
Power Consumed (KWH/1000 G)	116	34.2

The values of apparent effluent concentration given in Table 1 were determined by continuous measurement of the electrical conductivity of the effluent treated water. At low effluent concentrations this provides a sufficiently accurate measurement of actual concentration, i.e. within an error of about 10%, the error at 5 p.p.m concentration thus being

$\pm \frac{1}{2}$  p.p.m. To determine the effect of the cell on the pH of the water under treatment, a series of runs was conducted in the cell to produce effluents having various values of conductivity, the influent and effluent pH being measured in each run. As indicated in Table 3, the pH of the water was reduced in each case:

TABLE 3

Influ-ent pH	Efflu-ent pH	$\Delta$ pH	Effluent Conductivity ( $\mu$ mhos)
6.20	3.20	-3.00	250
6.52	4.00	-2.52	160
5.99	4.09	-1.90	100
6.10	4.52	-1.58	24
5.91	5.50	-0.41	8
5.75	5.02	-0.73	11
5.75	4.91	-0.84	30
5.35	3.88	-1.47	101
5.82	3.01	-2.81	150

## EXAMPLE II.

The bed of ion-exchange resin in the treating chamber of the above-described cell was replaced with a bed containing 30% cation-exchange resin and 70% anion-exchange resin. A further series of runs was then performed, again with water containing dissolved  $\text{Na}_2\text{SO}_4$ , following the procedure set forth above in Example I for runs I through VI.

In each run the cathode current density was maintained at a constant value of 10 amp./ft.<sup>2</sup> (the total current through the cell being 2.62 amps.), and the effluent concentration was determined by flame spectrophotometry. Data measured in these runs, together with calculated values of per cent demineralization, power consumption, and coulomb efficiency, are set forth in Table 4:

Run	VII	VIII	IX	X	X
Influent conc. (p.p.m.)	463*	488*	500**	500**	500**
Effluent conc. (p.p.m.)	103	68.6	20	13.3	7.7
Equilibrium Flow Rate (G.P.H.)	3.2	2.85	2.06	1.81	1.58
Voltage (v)	25.5	28.0	34.0	39.5	45.5
Flow rate, Cathode Stream (ml/sec)	2.66	2.64	2.26	0.57	2.40
Flow rate, Anode Stream (ml/sec)	1.23	1.12	1.05	1.03	0.90
pH (Feed)	5.86	6.08	6.19	6.27	5.98
pH (Product)	3.75	5.80	8.42	8.65	6.40
pH (Cathode Stream)	11.63	11.27	11.36	11.82	11.38
pH (Anode Stream)	2.05	1.95	2.20	2.31	2.28
Effluent Temp. (°C.)	24	24	27	23.5	22.8
Demineralization (%)	77.7	86.0	96.0	97.5	98.4
Power Consumed (KWH/1000G)	20.9	25.5	43.3	57.2	75.5
Coulomb Efficiency (%)	63.2	65.3	53.8	48.0	42.4

\* determined by flame spectrophotometry  
 \*\* nominal solution

5 In run VII, measurements were made of the Na<sup>+</sup> concentration in the anolyte and the catholyte solutions: the Na<sup>+</sup> concentration was found to be 165 p.p.m. in the anolyte and 280 p.p.m. on the catholyte.

With the treating chamber bed containing 30% cation-exchange resin and 70% anion-exchange resin, it was found that for low

values of effluent concentration the pH of the water under treatment was increased during demineralization. This result will be apparent from Table 5, which sets forth measured values of influent and effluent pH for runs VII—XI and other runs through the cell containing the latter bed, at various values of effluent conductivity:

TABLE 5

Run	Influent pH	Effluent pH	Change in pH	Effluent Conductivity ( $\mu$ mho)
VII	5.86	3.75	-2.11	230
—	5.86	3.97	-1.89	215
—	5.86	4.49	-1.37	185
VIII	6.08	5.80	-0.28	143
—	6.08	9.25	3.17	126
—	6.08	9.52	3.44	98
IX	6.19	8.42	2.23	40
—	6.19	9.19	3.00	50
X	6.27	8.65	2.38	24
—	6.27	9.20	2.93	30
IX	5.98	6.40	0.42	12
—	5.98	6.31	0.33	10
—	5.98	6.50	0.52	9

Due to the increase in proportion of anion-exchange resin (which is less conductive than cation-exchange resin), the total voltage across the cell is greater when the treating bed contains cation and anion-exchange resins in a 30-70 ratio than when the bed contains the resins in equal parts as in Example I above. This increase in voltage, as a function of effluent conductivity, is indicated in Table 6, which summarizes data derived from curves obtained by plotting experimentally determined values of voltage against effluent conductivity, for runs through each of these beds with a current density of  $10^{4\text{m}}/\text{ft}^2$ , total current of 2.62 amps., and influent concentration of 500 p.p.m.  $\text{Na}_2\text{SO}_4$ .  
5 10 15

TABLE 6

Effluent Conductivity ( $\mu \text{ mhos}$ )	Voltage (50% — 50% bed)	Voltage (30% — 70% bed)	Voltage Increase (%)
250	16.5 v.	24.8 v.	50.3
150	18.0	28.0	55.6
100	19.2	30.5	58.8
50	21.4	35.0	63.6
25	23.5	39.7	69.0
10	26.2	45.4	73.3

## EXAMPLE III.

By way of further illustration of the invention, a larger cell, for demineralization of naturally occurring hard water, sodium chloride solution or any other aqueous electrolyte, was constructed as shown in Figs. 1—2. In this cell the inner cathode was a 12" long by  $2\frac{1}{4}$ " outside diameter stainless steel tube. The cation tubular permeable membrane was  $5\frac{1}{2}$ " in diameter, 12" long and 40 mils thick; the anion tubular permeable membrane was 6" in diameter, 12" long and 40 mil thick. The outer anode was a graphite pipe  $7\frac{3}{4}$ " in inside diameter,  $9\frac{1}{4}$ " in outside diameter and 12" long.  
20 25 30 35 40 45

The mixed bed in the treating chamber was provided by a mixture of 30% cation resin and 70% anion resin. The cation resin was Amberlite IR-120 and the anion resin Amberlite IRA-400, both manufactured by Rohm & Haas Co. The catholyte bed consisted of Amberlite IR-120 cation resin and the anolyte bed of Amberlite IRA-400 anion resin.

A series of runs was performed in the above described cell under various operating conditions. In each case the influent water to be treated was a natural hard water of the following composition:  
45

Cations (ppm as $\text{CaCO}_3$ )		Anions (ppm as $\text{CaCO}_3$ )	
Sodium	= 102	Bicarbonates	= 122
Potassium	= 21	Sulfates	= 79
Calcium	= 48	Chlorides	= 19
Magnesium	= 62		

It will be understood from the term "ppm as  $\text{CaCO}_3$ " that the foregoing values of concentration of the various cations and anions specified are expressed as equivalent concentrations of calcium carbonate in parts per million,  
50 55

this being the standard measure of water hardness.

For each run, the electric current was set and maintained at a constant predetermined value and the water to be demineralized was

passed in continuous flow through the treating chamber. The effluent of the apparatus was analyzed for total hardness ( $\text{Ca}^{++}$  plus 5  $\text{Mg}^{++}$ ) in order to test the cell as a water softener.

In all these runs, the direction of flow of the anolyte and catholyte solutions in the electrode chambers was upward. To test cell performance under various flow conditions, the flow through the treating chamber was directed upwardly in some runs and downwardly in others; also, in some runs the anolyte and catholyte flows were arranged in series (i.e. the

same flow was passed successively through the anode and cathode chambers), while in other runs the anolyte and catholyte flows were arranged in parallel (i.e. with separate flows through the anode and cathode chambers). 15

The data obtained, together with calculated values of the current efficiency and power consumption are set forth in Table 7. In table 20 7, the values of influent hardness and effluent hardness represent the sum of the concentrations of calcium ions and magnesium ions present, expressed as equivalent concentrations of 25 calcium carbonate, in parts per million.

TABLE 7

Run	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI
Flow direction-treating chamber	U	D	D	D	U	D	D	D	D	D
Flow arrangement-electrode chambers	P	P	S	S	P	S	S	S	S	S
Current (Amps.)	3.0	3.0	3.0	3.0	3.0	3.0	6.0	5.0	6.0	6.0
Flow rate (Gal. per day)	182	182	182	182	256	256	400	400	466	542
Flow rate (Gal. per Hour)	7.6	7.6	7.6	7.6	10.7	10.7	16.7	16.7	19.4	22.6
Voltage (v.)	43.0	42.5	40.0	39.3	38.0	38.0	71	66	70	70
Influent hardness (ppm $\text{CaCO}_3$ )	135	125	125	131	135	130	130	130	130	130
Effluent hardness (ppm $\text{CaCO}_3$ )	55	46	40	49	74	55	44	57	50	53
Anode chamber flow rate (Gal. per Hour)	0.58	0.58	0.58	1.3	0.58	1.3	1.3	1.3	1.3	1.3
Cathode chamber flow rate (Gal. per Hour)	0.58	0.58	0.58	1.3	0.58	1.3	1.3	1.3	1.3	1.3
pH feed	7.8	8.0	—	8.2	7.8	8.2	—	—	—	—
pH product	6.4	5.8	—	7.0	7.2	6.6	—	—	—	—
pH catholyte	12.1	12.1	—	11.3	12.1	11.3	—	—	—	—
pH anolyte	2.4	1.9	—	1.9	2.0	1.9	—	—	—	—
Current Efficiency (%)	77.2	81.2	87.8	72.0	83.5	94.6	85.8	95.6	97.3	99.9
Power consumed (KWH/1000G)	17.0	16.8	15.8	15.6	10.7	10.7	26.1	20.2	21.6	18.6

Legend

- U = Upward flow
- D = Downward flow
- P = Parallel flow
- S = Series flow

**EXAMPLE IV.**

5 A further series of runs was then performed with water containing dissolved NaCl, using the same cell and following the procedure set forth in Example III. In all the runs in the present example, the flow through the treating chamber was directed downwardly, while the

flows through the anode and cathode chambers were directed upwardly and were arranged in series.

10 The data measured in these runs, together with calculated values of current efficiency and power consumption, are set forth in Table 8:

TABLE 8

Run	XXII	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII
Current (Amps.)	0.5	1.0	1.0	1.5	1.5	2.0	1.5
Flow rate (Gal. per day)	101	101	182	182	256	256	400
Flow rate (Gal. per hour)	4.2	4.2	7.6	7.6	10.7	10.7	16.7
Voltage (v.)	8.6	12.5	12.5	16.5	15.8	20.3	12.0
Influent concentration (ppm)	163	165	170	165	171	171	163
Effluent concentration (ppm)	95	70	110	89	110	107	117
Anode chamber Flow rate (Gal. per hour)	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Cathode chamber Flow rate (Gal. per hour)	1.3	1.3	1.3	1.3	1.3	1.3	1.3
pH feed	6.1	6.3	6.4	6.8	6.2	—	—
pH product	9.6	7.2	8.8	6.0	7.2	—	—
pH catholyte	8.3	7.8	7.2	9.2	9.9	—	—
pH anolyte	3.2	2.0	2.4	2.2	2.4	—	—
Current efficiency (%)	95.2	66.5	79.0	66.7	75.1	59.3	88.7
Power consumed (KWH/1000)	1.03	2.9	1.65	3.27	2.22	3.81	1.08

- 15 The foregoing examples illustrate the performance of cells in accordance with the invention for a variety of electrolytes, viz Na<sub>2</sub>SO<sub>4</sub>, natural hard water and NaCl. In these examples, a wide range of flow rates 35
- 20 (from 26 gal. per day in Example I, run I to 542 gal. per day in Example III, run XXI) was obtained at economical levels of power consumed. Current efficiencies approaching 40% were achieved in the cell of Example III and IV (see, e.g. Example III, run XXI and Example IV, run XXII), the average current efficiency in the latter two examples being of the order of 80% to 90%. Moreover, as will be apparent from a comparison 45
- 25 of run XIV in the cell of Example III (Table 7) with run VII in the cell of Example II (Table 4), use of the larger cell of Example

III afforded more than twice the flow rate attained in the smaller cell of Example II, with an increase of about 40% in current efficiency and a reduction of about 25% in power consumption per unit volume of water treated as compared to the run in the smaller cell, for similar conditions of total current, percentage demineralization and treating chamber bed composition.

50 In the operation of the above-described electrodialytic cells of the invention, as illustrated by the foregoing examples (Examples I and II) of deionization of water containing Na<sub>2</sub>SO<sub>4</sub>, it is found that by varying the ratio of anion-exchange resin to cation-exchange resin in the deionization chamber a control of the pH of the deionized effluent stream is obtained; i.e., addition of more anion resin

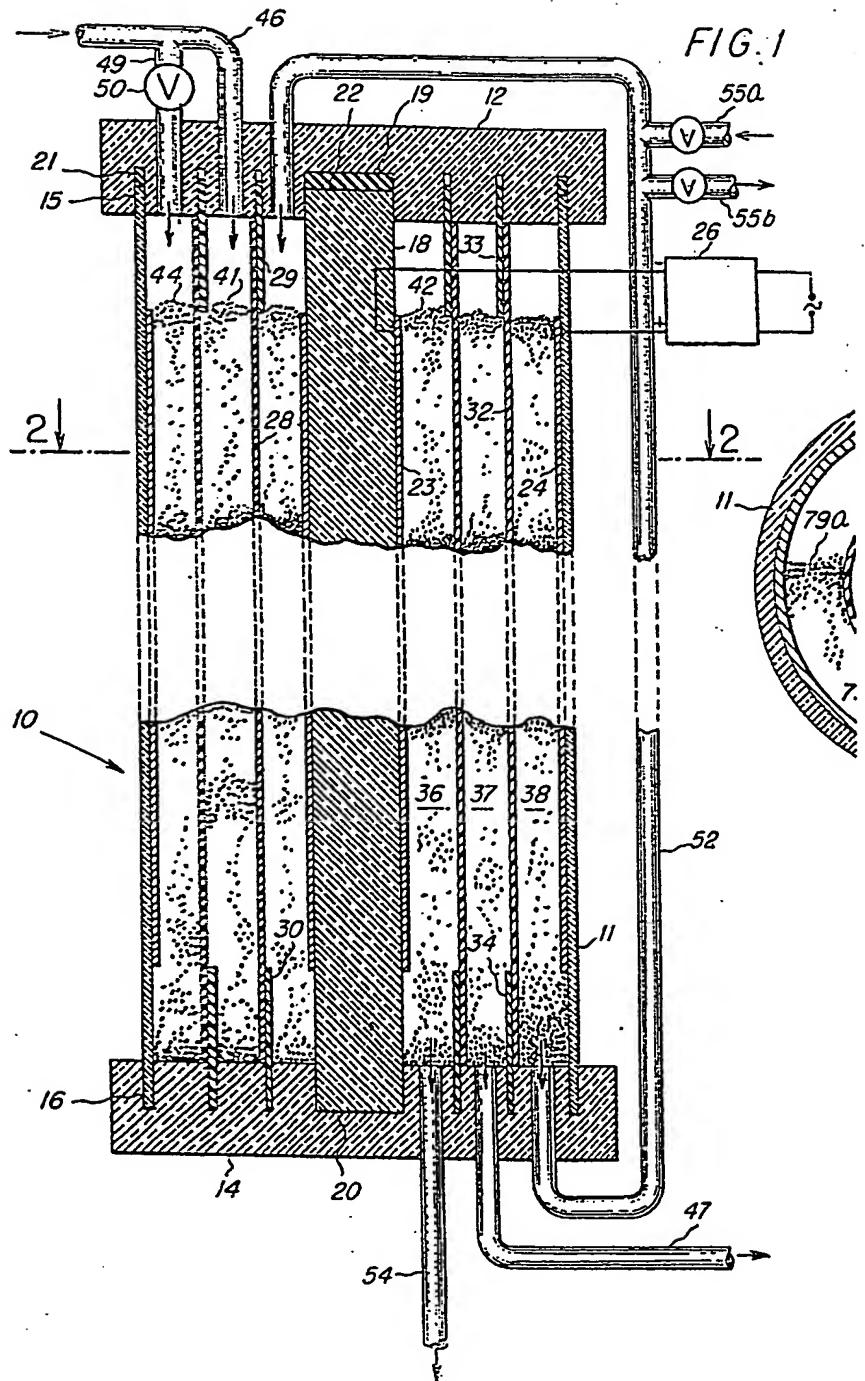
- than cation resin tends to increase the effluent pH, while addition of equal proportions of anion resin and cation resin tends to decrease the effluent pH. Thus, for given operating conditions, the relative proportions of cation and anion-exchange resins in the treating chamber bed may be selected to provide an effluent pH within a desired predetermined range.
- 10 WHAT WE CLAIM IS:—**
1. In a cell for effecting changes in concentration of ions in aqueous electrolytic solutions, in combination, an inner electrode; a hollow outer electrode concentrically surrounding said inner electrode in spaced relation thereto, said inner and outer electrodes laterally defining a cell region; a plurality of tubular permselective membranes including at least one cation-permselective membrane and at least one anion-permselective membrane, positioned in said region in concentric spaced relation to each other and to said electrodes to divide said region into a plurality of concentric chambers for receiving aqueous electrolytic solutions, said chambers including at least an inner electrode chamber contiguous to said inner electrode, an outer electrode chamber contiguous to said outer electrode, and an intermediate chamber defined between said one cation-permselective membrane and said one anion-permselective membrane; and a packed bed of divided solid ion-exchange material substantially filling one of said chambers.
  2. A cell according to claim 1, wherein the radial distance between said one cation-permselective membrane and said one anion-permselective membrane is substantially uniform around the cell.
  3. A cell as defined in claim 1 or 2, wherein said bed is disposed in said one intermediate chamber.
  4. A cell as defined in claim 1 or 2, wherein said bed is disposed in one of said electrode chambers.
  5. A cell as defined in claim 1 or 2, wherein each of said chambers is substantially filled with a packed bed of divided solid material.
  6. A cell as defined in any one of the preceding claims, wherein each of said beds comprises divided solid ion-exchange material.
  7. A cell as defined in any one of the preceding claims, wherein said packed bed of divided solid ion-exchange material substantially fills said one intermediate chamber and is adapted to provide both positive and negative mobile ions.
  8. A cell as defined in claim 7, wherein said packed bed comprises a mixture of cation-exchange resin particles and anion-exchange resin particles.
  9. A cell as defined in any one of the preceding claims, wherein each of said chambers is substantially filled with a packed bed of divided solid ion-exchange material, that
- one of said electrode chambers which is on the side of said intermediate chamber defined by said cation-permselective membrane being substantially filled with a packed bed of divided solid ion-exchange material adapted to provide positive mobile ions, and the other of said electrode chambers being substantially filled with a packed bed of divided solid ion-exchange material adapted to provide negative mobile ions.
10. A cell as defined in any one of the preceding claims, which is axially vertical, and including means for introducing water to an upper locality of said intermediate chamber and means for discharging water from a lower locality of said intermediate chamber to provide downward flow of water through said intermediate chamber.
11. A cell as defined in claim 10, wherein said ion-exchange material comprises ion-exchange resin of a particle size approximating that selected by passing through a 50 mesh screen, as herein defined.
12. A cell as defined in any one of the preceding claims, including means for supplying water to that one of said electrode chambers which is on the side of said intermediate chamber defined by said anion-permselective membrane, means for circulating water from said one electrode chamber to the other of said electrode chambers, and means for discharging water from said other electrode chamber.
13. A cell as defined in any one of the preceding claims, wherein said cation-permselective membrane is on the inner side of said intermediate chamber.
14. A cell as defined in any one of the preceding claims 1 to 12, wherein said cation-permselective membrane is on the outer side of said intermediate chamber.
15. A cell as defined in any one of the preceding claims, wherein said cell further includes power supply means for effecting passage of direct current through said chambers between said electrodes in such direction as to promote migration of cations into said intermediate chamber through said cation-permselective membrane.
16. A cell as defined in any one of the preceding claims 1 to 14, wherein said cell further includes power supply means for effecting passage of direct current through said chambers between said electrodes in such direction as to promote migration of cations out of said intermediate chamber through said cation-permselective membrane.
17. A cell according to any one of the preceding claims, wherein said packed bed comprises a mixture of anion-exchange resin particles and cation-exchange resin particles in relative proportions selected to provide an effluent pH, for the aqueous electrolytic solution passed through said one intermediate chamber, within a predetermined range.
18. A cell substantially as hereinbefore de-

- scribed with reference to the accompanying drawings.
19. A process for effecting transfer of ions between a first aqueous electrolytic solution and second and third aqueous electrolytic solutions, comprising passing said first solution through a first annular chamber, while passing said second solution through a second annular chamber concentric to said first chamber and separated therefrom by a first tubular membrane selectively permeable to ions of one charge type, one of said first and second chambers being substantially filled with a packed bed of divided solid ion-exchange material, and while passing said third solution through a third annular chamber which is concentric to said first chamber and on the side thereof opposite to said second chamber and separated from said first chamber by a second tubular membrane selectively permeable to ions of charge type opposite to said one charge type, and while passing direct electric current radially through said chambers and said bed in a direction effective to promote migration of ions of said one charge type from said bed through said first membrane.
20. A process according to claim 19, wherein in said packed bed of divided solid ion-exchange material provides both positive and negative mobile ions.
21. A process according to either of claims 19 or 20, including the steps of continuously supplying water to said third chamber to constitute said third aqueous electrolytic solution, circulating said solution from said third
- chamber to said second chamber to constitute said second solution and discharging said second solution from said second chamber.
22. A process according to any one of the preceding claims 19 to 21, including the further steps of continuously introducing water to an upper locality of said third chamber, circulating water from a lower locality of said third chamber to an upper locality of said second chamber, and discharging water from a lower locality of said second chamber.
23. In a cell for effecting changes in concentration of ions in aqueous electrolytic solutions, in combination, an inner electrode; a hollow outer electrode concentrically surrounding said inner electrode in spaced relation thereto, said inner and outer electrodes laterally defining a cell region; a cylindrical permselective membrane positioned in said region in concentric spaced relation to said electrodes to divide said region into two concentric chambers for receiving aqueous electrolytic solutions; and a packed bed of divided solid ion-exchange material substantially filling one of said two chambers.
24. A process for effecting transfer of ions between a first aqueous electrolytic solution and second and third aqueous electrolytic solutions substantially as described.
25. A solution of ions whenever prepared by the process substantially as described.

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FIG. 1



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FIG. 1

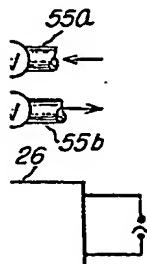
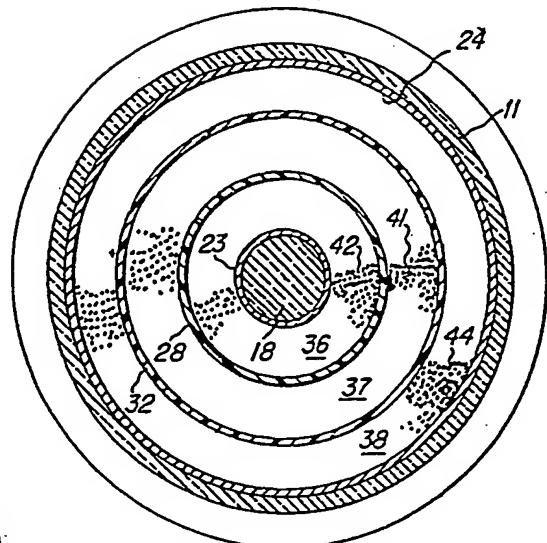


FIG. 2



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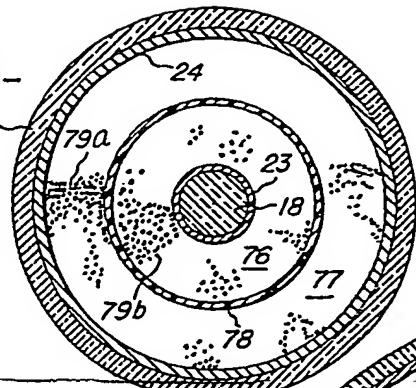
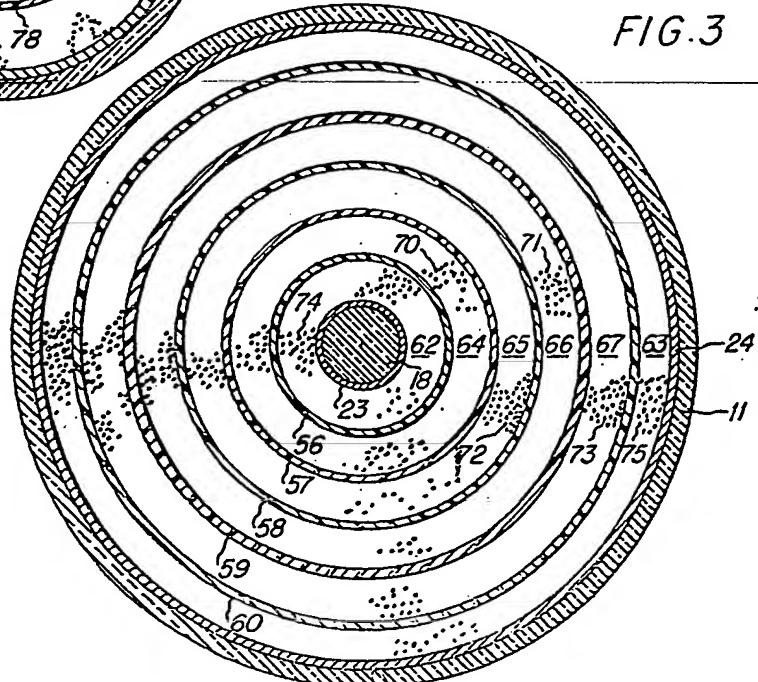


FIG. 3a

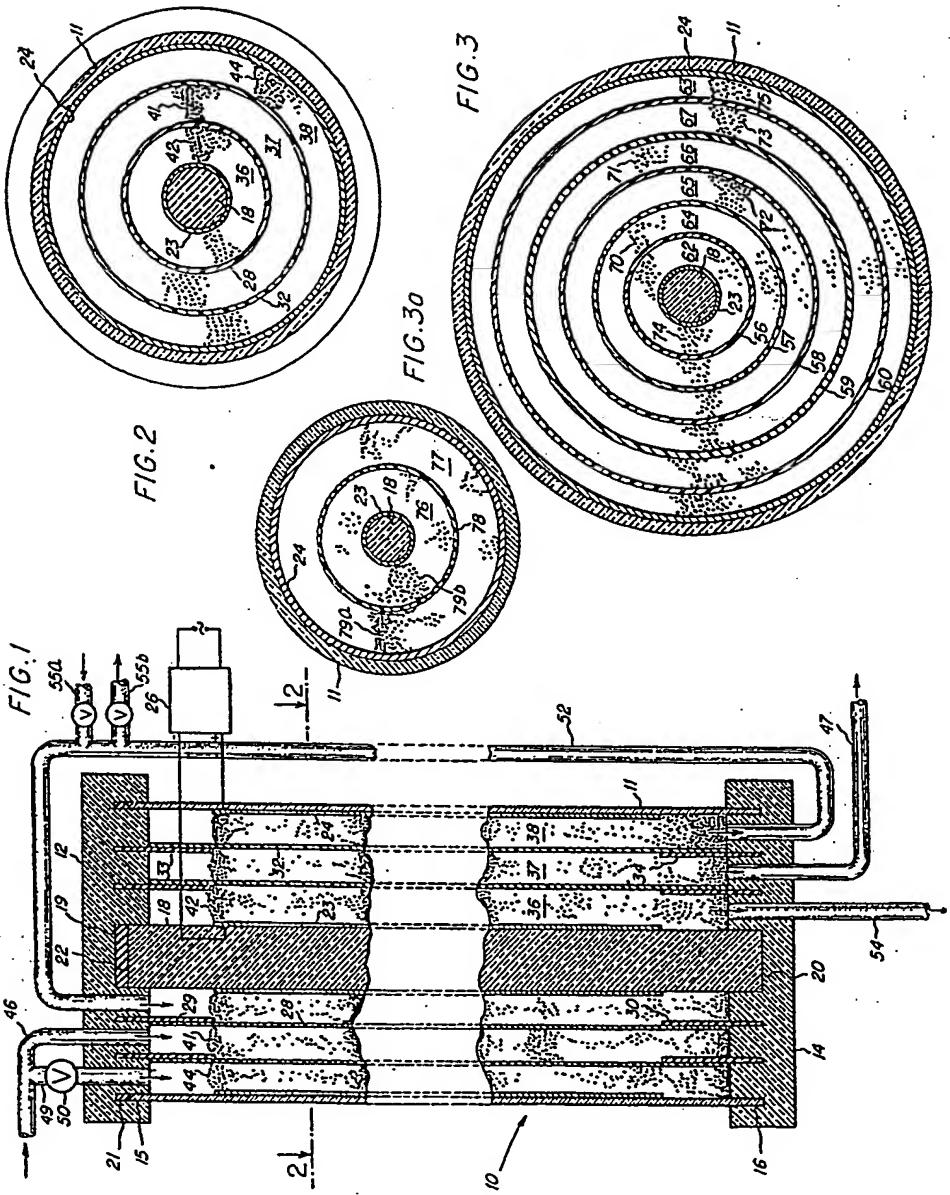


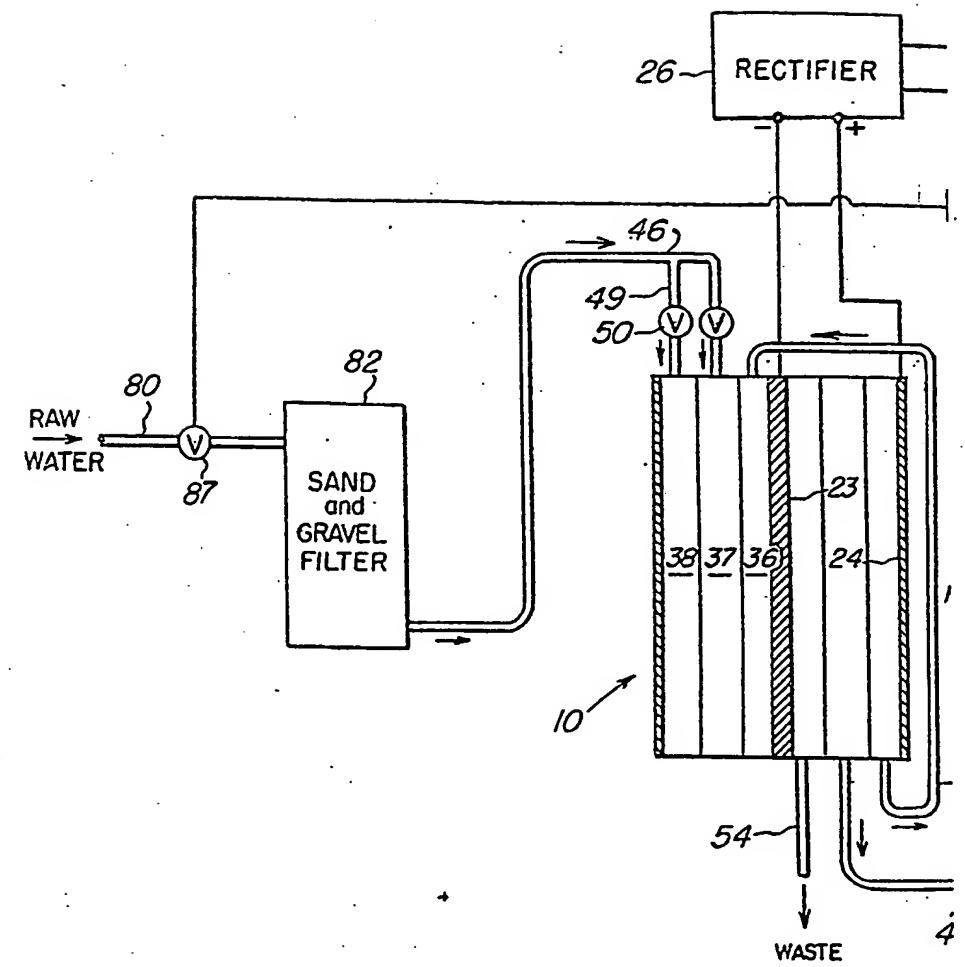
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FIG. 3



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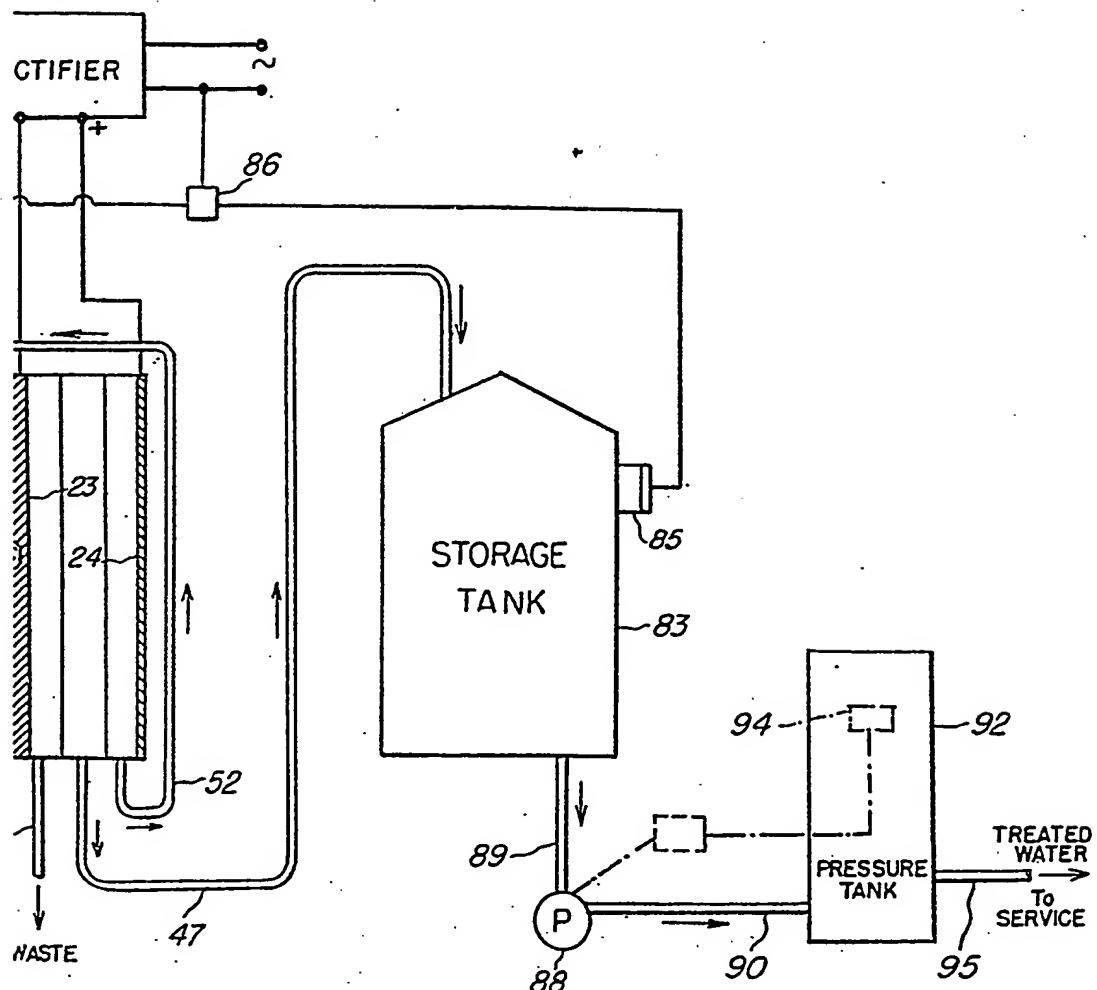


FIG. 4

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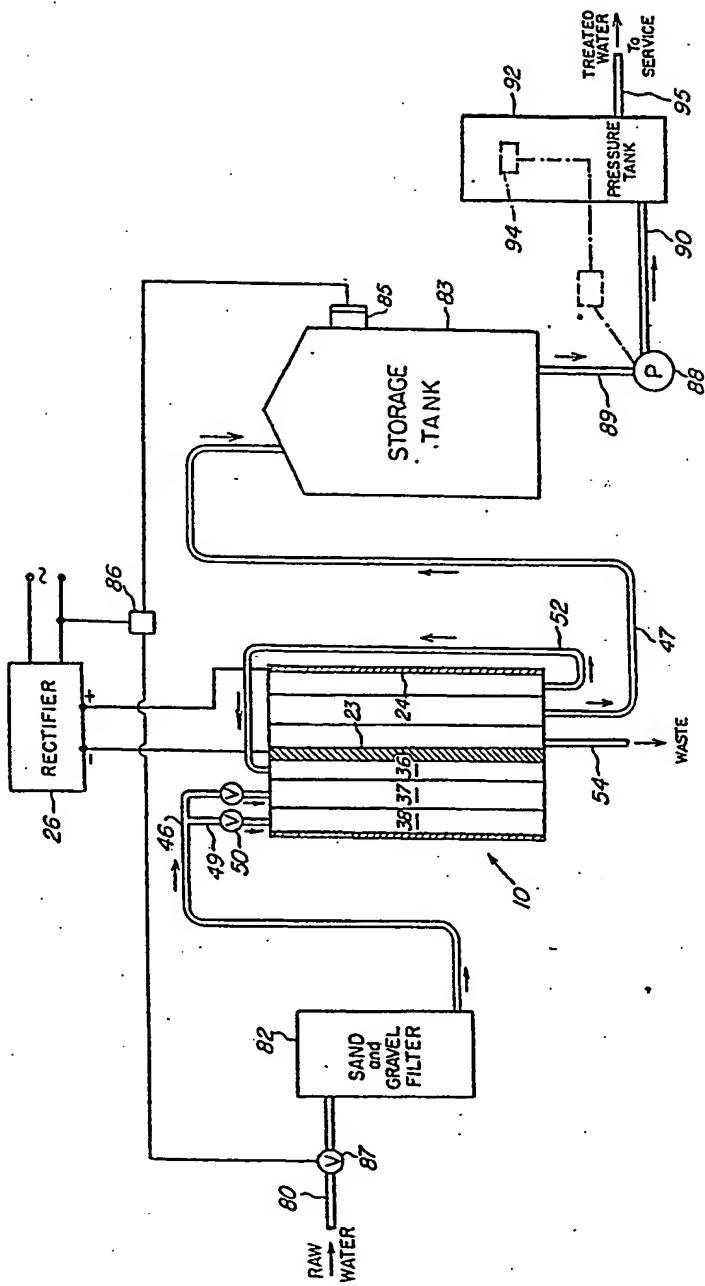
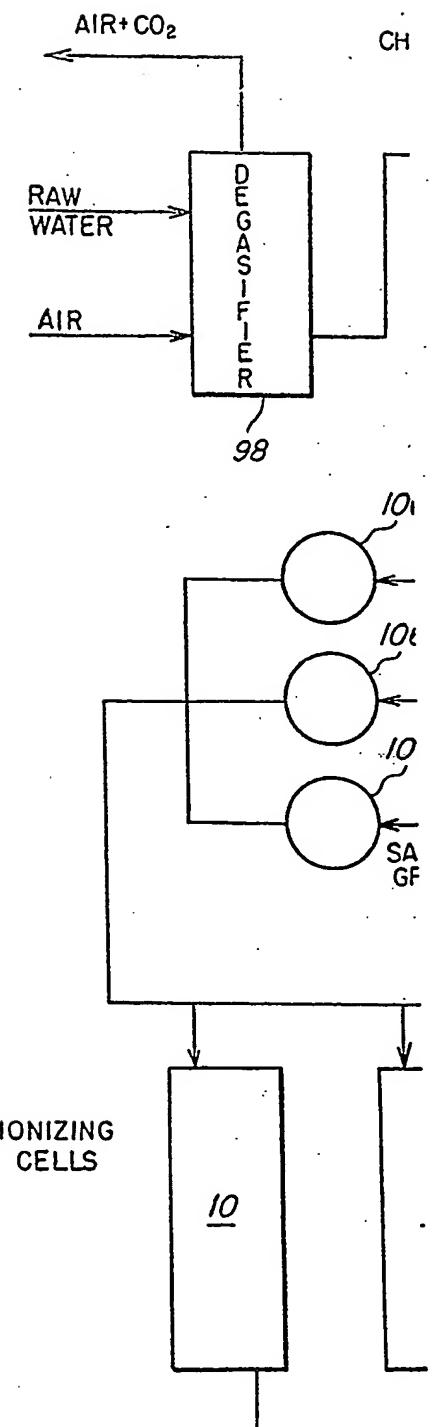


FIG. 4

FIG. 5

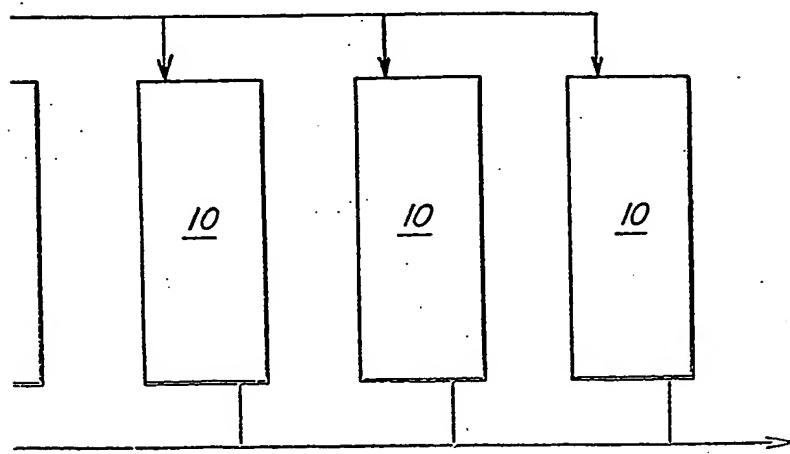
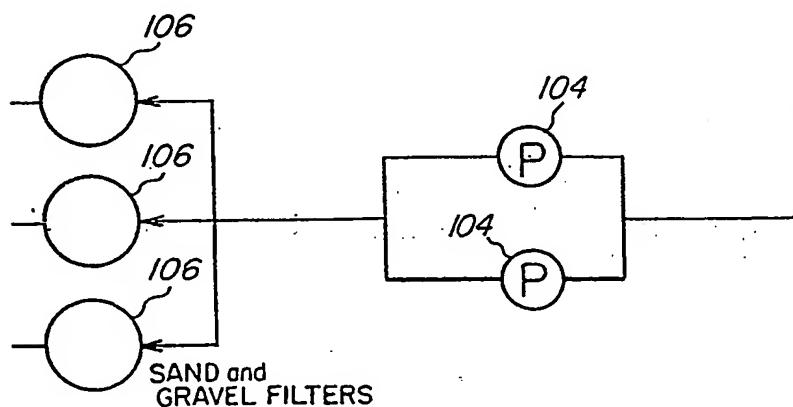
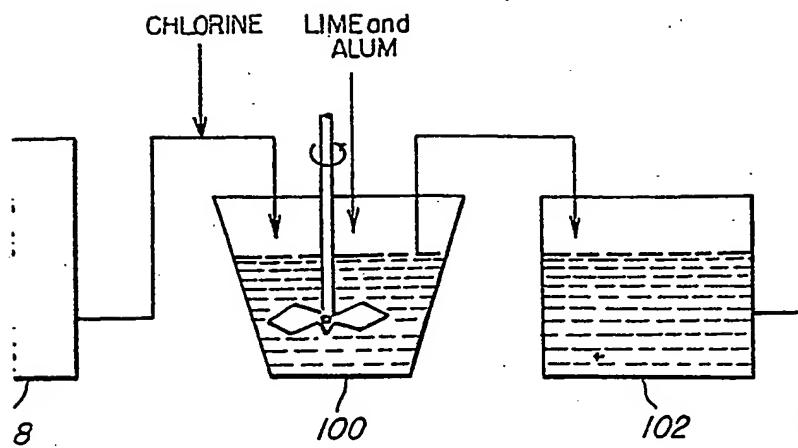


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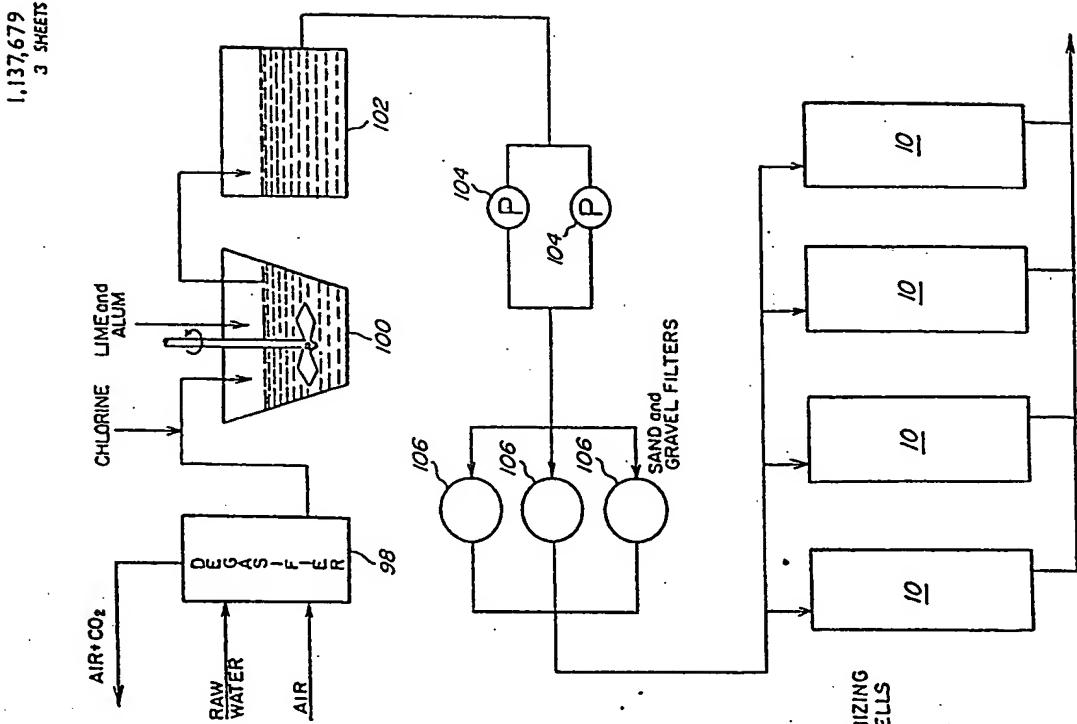


FIG. 5